FILE

Zircoa

ZIRCONIUM
OXIDES
AND
HIGH
TEMPERATURE
MATERIALS

Electronic/Technical
Ceramic Manufacturing

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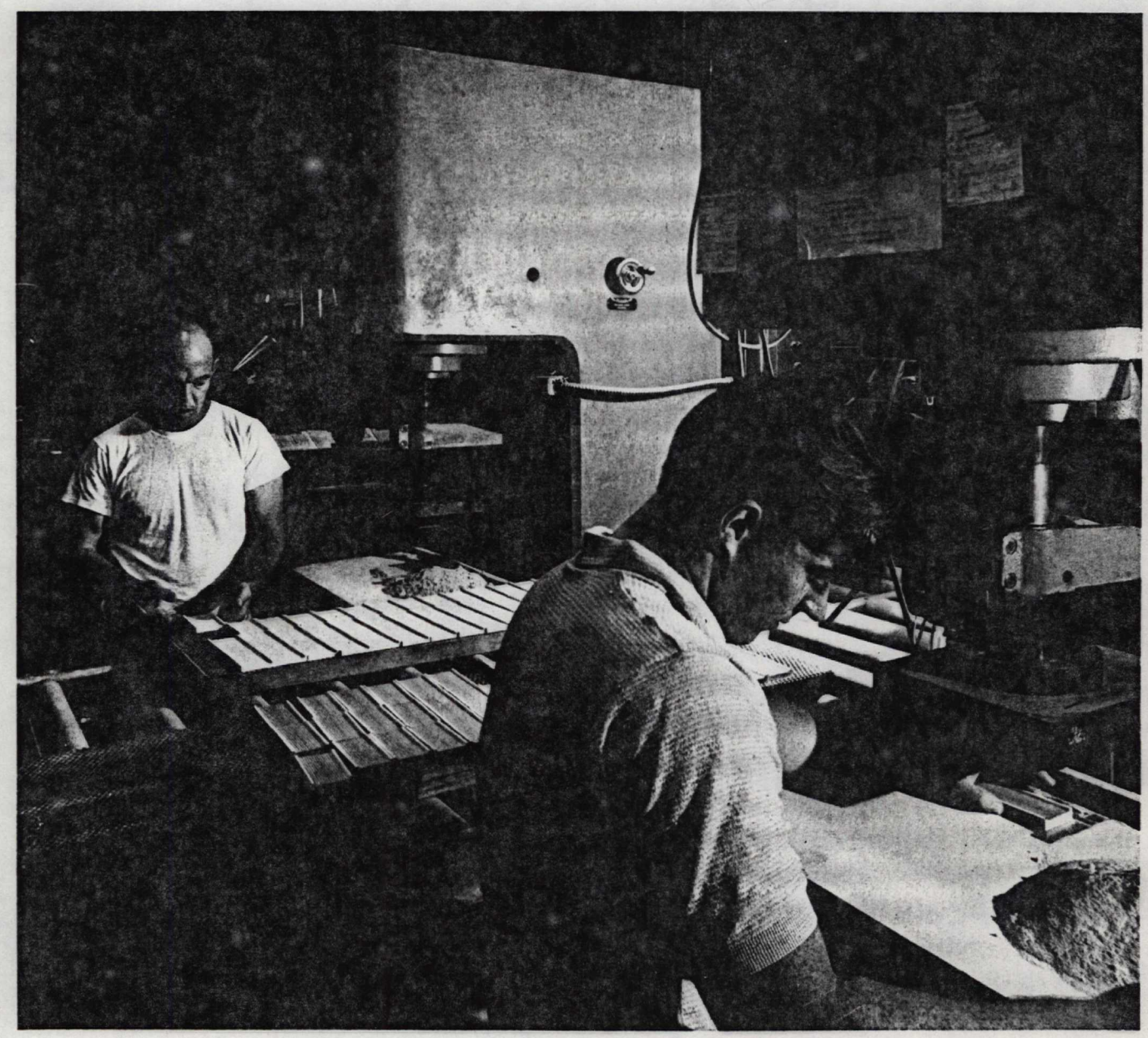
MBC

ZIRCONIUM CORPORATION OF AMERICA
P. O. Box 9583 • Solon, Ohio 44139 • Phone 216 248-6191
Solon

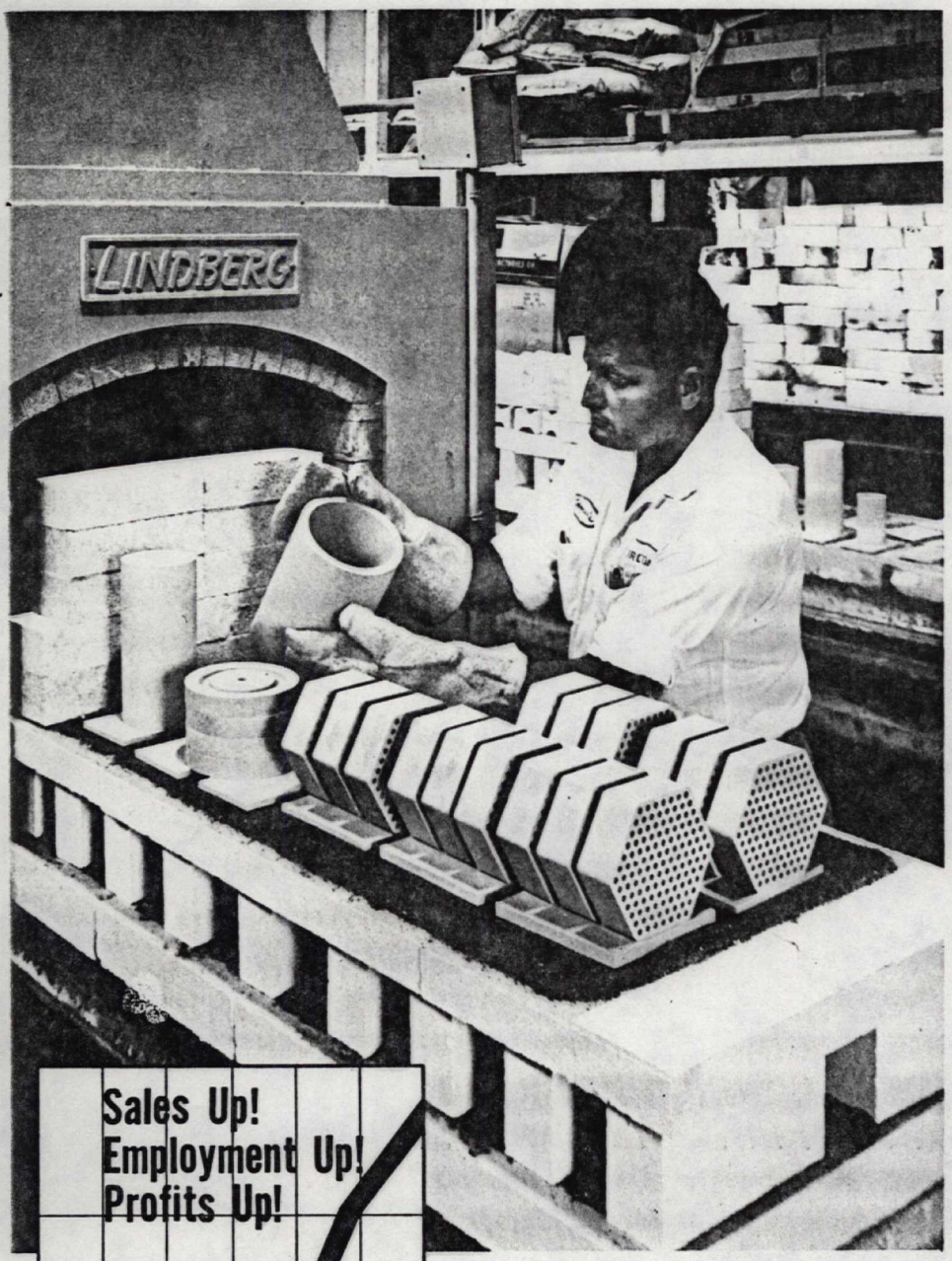
ETC

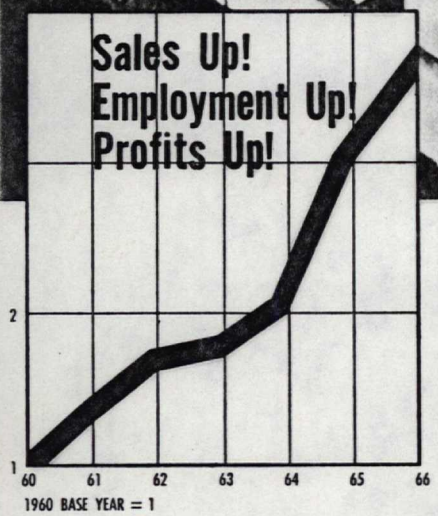
Electronic/Technical Ceramic Manufacturing



Pressing setter plates at the Solon, Ohio, plant of Zirconium Corporation of America. The company's growth, processing techniques and material investigation techniques are covered in two articles in this section.

Devoted to Reporting Progress in Compositions, Processing Techniques & Devices





New Markets Mean Growth for Zircoa

By **R. Francis Tatnall**
Editor

New applications for zirconium oxide have led to rapid growth at Zirconium Corporation of America during the past seven years. The Solon, Ohio firm has practically quadrupled its sales volume, doubled the size of its plant and more than doubled its work force since 1960. During the period 1960-66 sales grew 40% per year, while profits increased at a rate of 30% per year. By August, 1967, Zircoa will have doubled the value of its assets over August, 1965—growth based on internally generated financing.

The reasons behind this rapid growth?

E. C. Sargent, Zircoa's president and general manager, attributes the company's growth pattern to two major factors:

1. The fact that almost any process operates more efficiently at a higher temperature,

2. The company's efforts in finding new applications for its materials and developing new materials to meet the requirements of specific applications.

Sargent cites changing attitudes among refractory users toward higher productivity, higher quality and lower costs for their end products, even if the initial cost for refractories used is higher, as a major factor in Zircoa's growth and plans for the future. According to Sargent, 60% of the growth reported in this article is based on new applications and new materials. Increased use of zirconium oxide grain and fabricated parts in established applications accounts for 40% of the company's growth.

Operations Started—1954

Zircoa was incorporated in 1952 and the original raw material plant was constructed and in operation by 1954. The raw material plant produces zirconium oxide from zircon ore and limestone using a process based on a series of patents resulting from work done by Dr. R. A. Schoenlaub and associates. Shortly after beginning operations and until 1960, Zircoa operated as a subsidiary of the Oliver Tyrone Corporation of Pittsburgh. In 1960 Zircoa's assets were purchased by a group that included nine employees and the firm has been an entirely independent company since that time.

To broaden its product base and develop additional markets, Zircoa began adding facilities for fabricating zirconium oxide into a variety of shapes and organized a research and development department in 1957.

Raw Material Production

Zirconium oxide is produced by calcining zircon and limestone at temperatures up to 2600 F in a 68′ long 36″ I.D. rotary kiln[1]. Calcining rate for the kiln depends on the raw material mix and the type of zirconia required, varying between 500-1000 pounds per hour.

Zircon and limestone materials are mixed with organic and inorganic

Opposite page: Removing ware from tunnel kiln at Zircoa.

binders in 1000 pound batches in a Simpson Muller mixer. After the materials are dry mixed, a 10% addition of tempering liquid is made and blended in with the muller mixer. The mixer dumps into a surge hopper that feeds to a Bonnot extruder. From the multi-orifice die on the extruder, rod-shaped pieces fall into a rotating drum that produces pellets approximately ½" in diameter. Undersize pellets are screened out at the exit end of the pelletizing drum.

A Prab drying conveyor transports pellets from the exit end of the pelletizing drum to the rotary kiln entrance, using waste heat from the kiln to dry the pellets enroute. The entrance end of the conveyor is maintained at 200 F, while the exit temperature is 400 F.

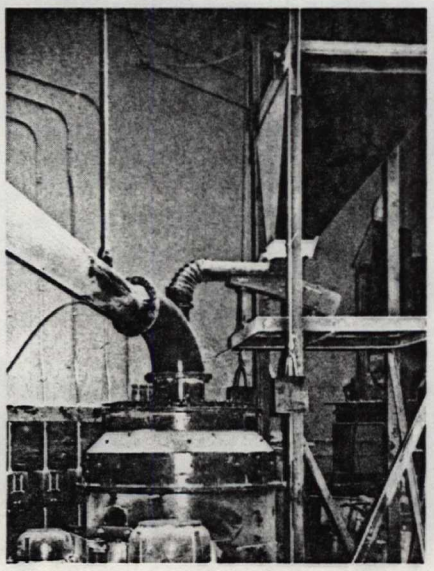
Rotary kiln temperature is recorded continuously based on radiation pyrometer readings, but temperature control is manual, based on observation of the behavior of the material in the kiln. The hot zone of the kiln is lined with mullite refractories.

Kiln discharge is water quenched and is fed to a roll crusher by a drag chain conveyor. Crushed clinker is stored in bulk in bins with capacity of 750,000 pounds. Material is moved to and from storage bins with a front-end loader attachment on a fork lift truck.

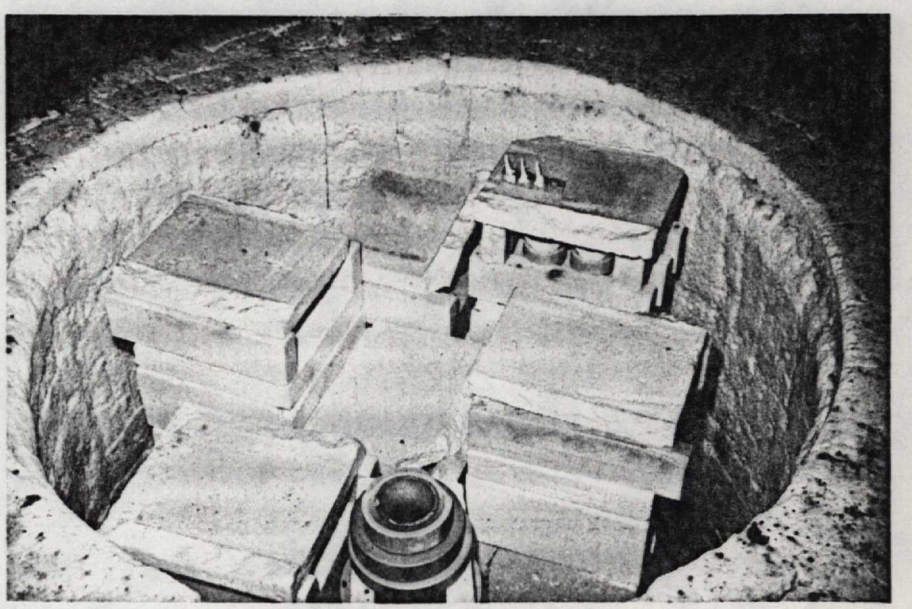
Leaching Process

Crushed clinker is wet ground to −200 mesh in a ball mill to prepare it for acid leaching. An Exact Weight feeder system using two vibratory

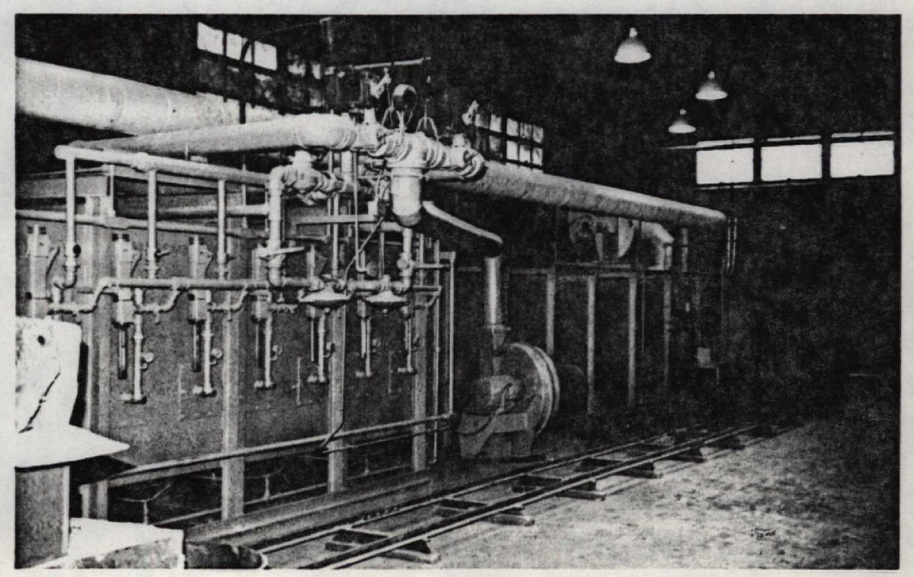
Below: Grog is ground in this vertical impact pulverizer.

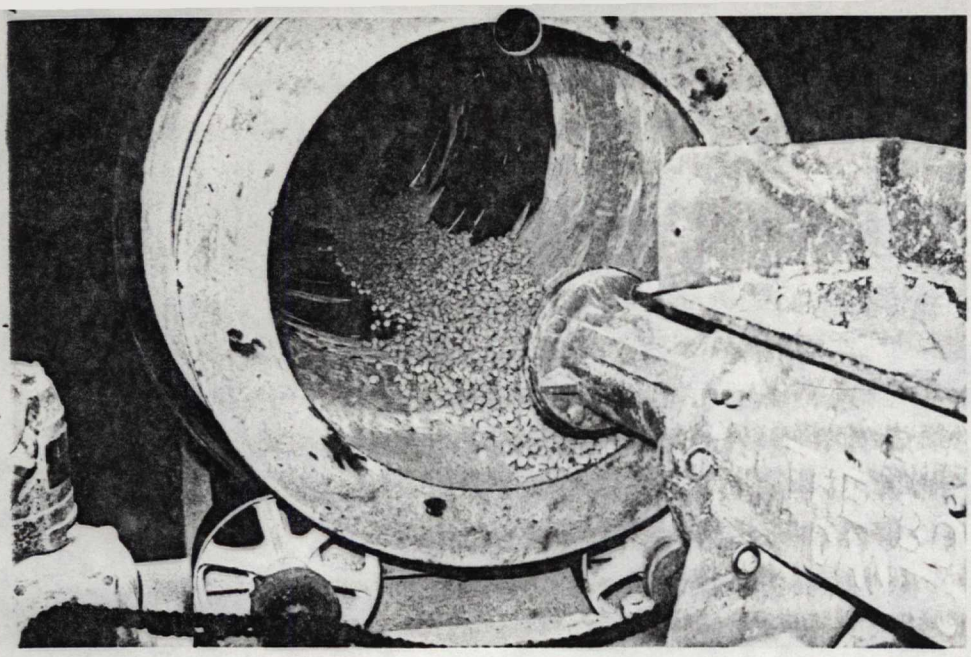


Above: Part of the slip-casting department.
Below: This pot furnace is used for firing slip-cast tubes and special compositions.



Below: Side view of tunnel kiln at Zircoa.





Extruded slugs are rounded in this rotating drum.

feeders meters small batches of calcine to the ball mill at one minute intervals. Batches are weighed to an accuracy of ±0.1%.

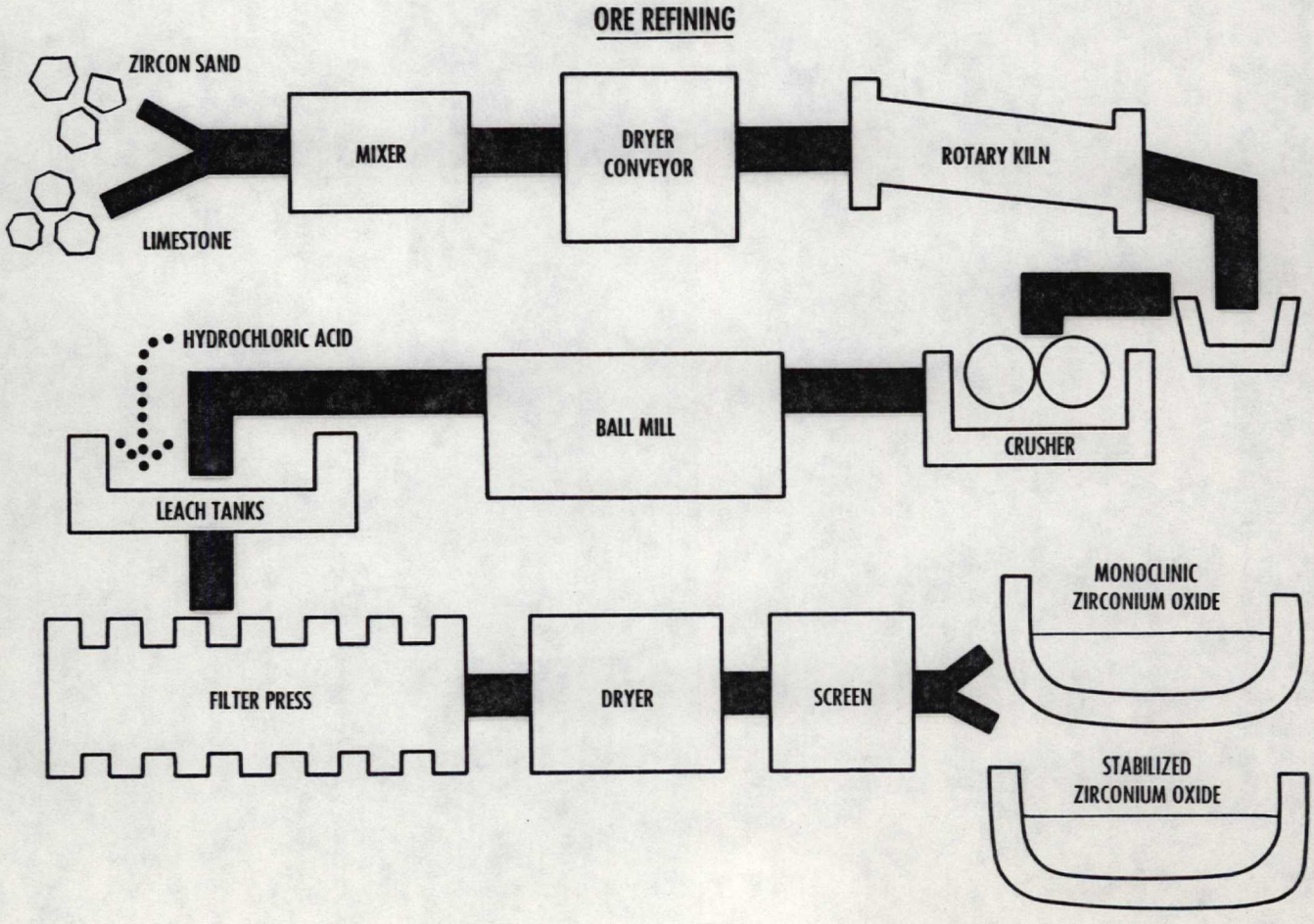
Undersize material (−200 mesh) is pumped to one of three 2500 gallon reaction tanks agitated by Lightnin' mixers. Clinker slurry is leached with a hydrochloric acid solution in the reaction tanks to dissolve the soluble calcium silicate formed in the rotary kiln. The leaching action is instantaneous, occurring as soon as contact is made in the reaction tank.

In production, three tanks are leached and fed to one of five Sperry filter presses for separation of the zirconium oxide. Two filter press loads are leached a second time and filter pressed again to make up a batch. The batch is neutralized in the filter press and dried at 1000-1200 F in a gas fired drier. A 10,000 pound rotary blender combines batches to provide lot number designations for raw material quality control purposes. Filtrate is neutralized with lime and pumped to a settling pond adjacent to the plant.

Grog Production

For some applications the zirconium oxide produced by the leaching process must be fired to 3250 F to produce high-fired zirconium oxide grog. To produce the required grog, zirconium oxide is extruded and cut into brick-like shapes called dobies and fired in pot furnaces to the desired temperature.

Fired dobies are crushed and screened to particle size specification. A recently installed grog sizing system consists of a Pennsylvania Crusher vertical impact pulverizer fed by a Syntron vibratory feeder and serviced by a Sly dust collector. The pulverizer reduces grog particle size by impacting



material against a layer of the material being ground. Properly sized material is removed by a cyclone. According to the operators, adjustments on the pulverizer (speed, air flow, slinger speed, vane angles, and feed size) permit grinding to specification. The grog sizing facility is also equipped with a Sprout Waldron gyratory sifter and a Stearns magnetic separator.

Fabrication

Raw materials are delivered to the fabrication department separated by particle size and are batched by particle size fractions to meet the specifications for the product being fabricated. Two Clearfield muller mixers blend the raw material fractions and binders for extrusion, dry pressing and isostatic pressing.

Stokes, Denison, Wilson and Hannifin presses range from 4 to 90-tons in capacity. Crucibles and tubes are pressed to dimension from weighed mold charges on the Wilson Arbor press to produce the desired fired density. Setter plates in twenty different sizes are pressed on the Denison presses. The Stokes rotary press is used to produce small flat shapes.

Slips for casting are produced in a Southwestern Engineering vibratory mill charged with zirconia media. The media are reported to have 1½ times the density and three times the wearing life of aluminum oxide media. A controlled temperature and humidity room is provided for drying slip cast ware and molds.

Tubing is extruded on a small F-R-H auger extruder and a hydraulic extruder built by Zircoa. An Autoclave Engineers isostatic press installed in the research and development department is used for some production fabrication work.[2]

Large shapes are formed by thixotropic casting in plaster molds on vibrating tables, using the company's castable compositions.

Die nibs, used for extruding metals, are dry pressed, machined to tolerance in the green state, fired, and diamond machined to specification in the fired state.

Firing

Production firing equipment at Zircoa includes an 80′ Lindberg tunnel kiln that fires to 3250 F or cone 35 down, eight box kilns equipped with burners that supply 3.6 million Btu/hr., and six pot furnaces. The tunnel kiln has a setting area 20″ wide by 22″ high on four foot cars. Box kilns are controlled manually on a 72-hour firing cycle. One of the pot furnaces is used to hang-fire slip cast tubes and to fire special compositions.

Quality Control

In addition to the petrographic techniques for quality control described by A. G. King in this issue, a wet chemistry laboratory under the direction of J. T. Welter, technical service manager, performs the following functions:

1. Checks incoming raw materials and supplies the results to production personnel to guide batch formulation.
2. Analyzes rotary kiln clinker—three shift samples per day during continuous operation; hourly samples during start-up.
3. Analyzes every leached batch for silica content.
4. Conducts complete chemical analysis on the finished zirconia to determine end-use distribution.

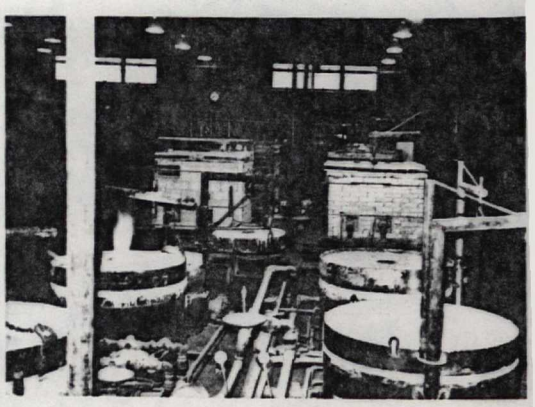
Research and Development

Zircoa's research and development department, headed by Paul J. Yavorsky, technical director, employs three engineers and seven technicians. The group is not set up for basic research; it is strictly an applied materials development group that believes more can be accomplished by removing or side-stepping deficiencies in known and reasonably economical materials than by pursuit of "wonder materials." The research and development group also produces prototype or "exotic" items for customers.

Developments during the past seven years include: High purity, impervious zirconia; High purity, impervious thoria; High purity, impervious hafnia; A gas-fired furnace for service to 4600 F; A zirconia castable system; Yttria stabilized zirconia refractories; High lime stabilized zirconia membranes for fuel cells; Zirconia porcelains for extrusion dies; Stabilized zirconia for glass melting applications; High density zirconia for hot extrusion dies; Zirconia media for dispersing pigments.

Marketing

Zircoa's marketing program, directed by Sydney Z. Gendel, sales manager, employs four technical service engineers and a field sales supervisor to uncover and develop new applications where the properties of zirconia can provide higher productivity, lower costs and higher quality in industrial processes. During 1966 a series of technical seminars devoted to the properties and capabilities of zirconium oxide was presented to engineering groups throughout the United States. This program is being expanded during 1967.



Zircoa's pot furnaces in the foreground; box furnaces are in the background.

The Future

Zircoa's growth pattern indicates that production requirements will soon strain the capacity of the refining operations. Although sales volume, profits, employment and plant facilities have all grown dramatically since 1960, and new applications for zirconia are developing rapidly, the production facilities depend on the output of the refining operation. The facility built in 1954 is still the company's only source of zirconium oxide and is now operating at twice its design capacity.

According to Sargent, the next big step for Zirconium Corporation of America will be an expanded refinery operation, designed to operate more efficiently so that prices for zirconia products can be reduced considerably. ■

References

1. Properties and High Temperature Applications of Zirconium Oxide; Paul J. Yavorsky; Ceramic Age, Vol. 78, No. 6, June 1962, pages 64-69.
2. Zircoa's Small-Size Lab Press Has Large-Scale 400-ton Capacity; Ceramic Age, Vol. 81, No. 9, September 1965, page 77.

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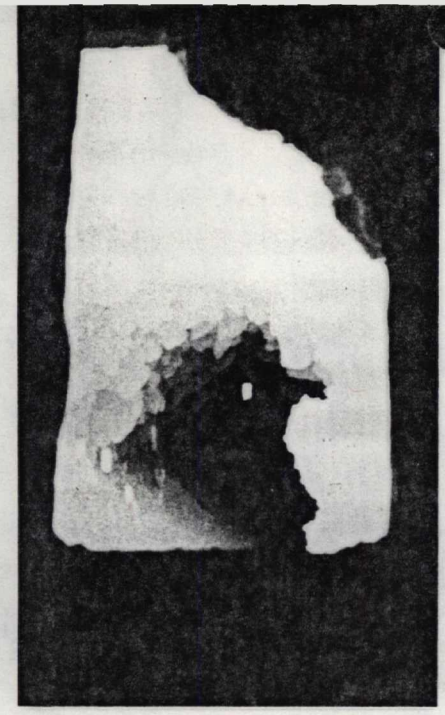

Figure 1: A look into Zircoa's rotary kiln at the clinker bed.

At Zircoa:

Microscopy Tells More About Processes . . . About Products

By **A. G. King** Zirconium Corporation of America

The ceramic producer is a close ally to the minerals producer, with much of his business concerned with very inexpensive raw materials: clay, feldspar, silica, magnesia, alumina, and even zirconia. In quantities, zirconia is obtainable at 99% purity (including Hf) for less than $0.60 per pound. Compared to cemented carbides at $10.00 per pound and refractory metals at $1.00 to $4.00 per pound, even a "premium" ceramic material such as zirconia is not particularly expensive by modern standards.

The close association with inexpensive materials has caused much of our industry to grow up in the "arts of technology" rather than in its science. This dependence on "art" is rapidly changing and Zircoa's addition of a well-equipped microscopic facility, with plans for expansion into X-ray diffraction and fluorescent analysis, is only indicative of an industry-wide trend toward greater refinement. It is no longer enough to just understand the physics and chemistry of ceramic materials, they must also be demonstrated and controlled during processing. The goal of the ceramic technologist is to convert physical knowledge into industrial action. The microscope is an excellent tool for obtaining knowledge, and, in demonstrating visually through photomicrography, production and management personnel accept that the observations are valid. Photomicrography de-personalizes the conclusions of the ceramic technologist—"You don't have to take my word for it; judge the evidence in the photograph for yourself."

Control of product quality and economics can be equated to product success in today's market. Manufacturers must understand their processes and impose process control measures that not only inform them when things are slipping, but feed back corrective measures to operating personnel. Microscopy is not new as a control tool in the production of ceramics. However, most of the control work using the microscope has been done on polished sections. Literature references to work using petrographic techniques (transmitted light) are rare.

There are good reasons why petrographic techniques should be more fully utilized. The petrographic microscope is the best way of studying ceramic microstructures and is often the best and most economical way of determining phase composition. In addition, the microscope can be used for determining grain sizes, particle sizes, identifying minerals, examining products that have been used, or products that have failed. The information about your products contained in a beam of transmitted light is much greater than that obtained from a reflecting surface. Your products will tell you about themselves, if you will only look at them in the right way.

Rather than attempt a complete systematic discourse on the use of the microscope in ceramics, it might be more helpful to examine three of Zircoa's recent experiences. These case histories are indicative of only some uses of microscopy. They are all concerned with thin-section studies, rather than polished sections, or ceramic powders.

Case History—I

The Problem: Marketing successes in the uses of zirconia powder have placed a strain on Zircoa's production facilities to supply this demand. While this is the sort of trouble a manufacturer likes to have, it does create quality problems within the plant, and appropriate controls must parallel the increases in throughput.

Zircoa was alert to this problem and one reason for establishing our microscope laboratory was to provide this necessary control.

The specific problem was to control the completeness of the lime-zircon reaction in the rotary kiln.

Analytical Examination: There wouldn't be a Zirconium Corporation of America if zirconium silicate (zircon) and calcium carbonate (limestone) didn't combine in a chemical reaction at a high temperature to produce zirconium oxide and calcium silicate. The two ingredient powders are well mixed, pelletized and reacted in a rotary kiln. Figure 1 shows a view looking into the kiln at the bed of "clinker" during the process of this chemical reaction. This raw product is crushed, pumped into digestion tanks where the calcium silicate is dissolved by mineral acid. The suspension of zirconia in the digestion liquor is filter pressed, washed, and then dried. Figure 2 shows the filter presses and lower portions of the acid tanks. After drying, it is batch blended to insure a reliable analysis over fairly large lots.

The batch composition is under close control, with individual lots of raw materials being analyzed chemically and blended to proper stoichiometric proportions.

Samples of the reacted clinker are prepared as thin sections for microscopic examination. Figure 3 is a

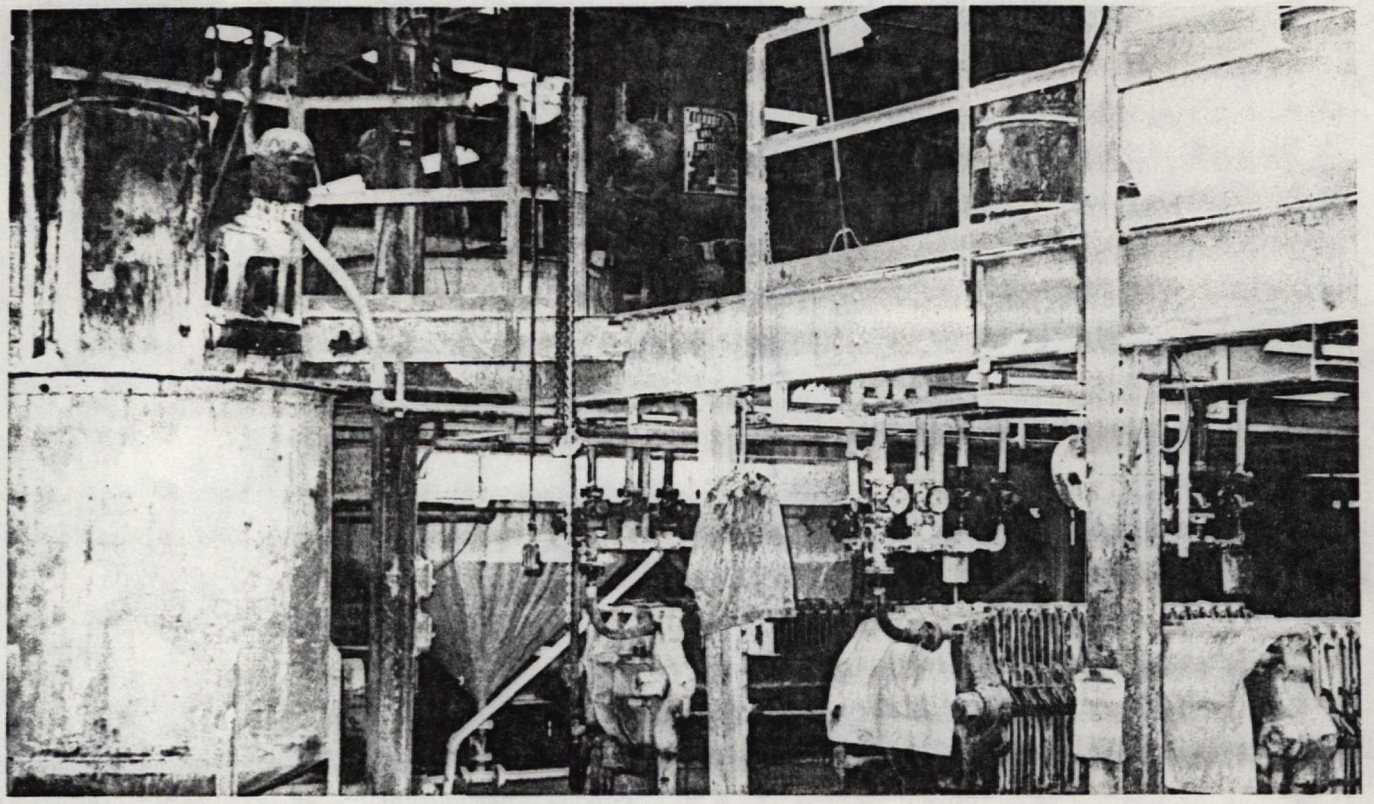

Figure 2: Digestion tanks (left) provide feed for filter presses (right).

view taken of an experimental clinker showing four "phases": unreacted zircon, zirconium oxide, calcium silicate, and pores. Under the petrographic microscope, the control problem immediately became obvious; the reaction in the rotary kiln must be complete or unreacted zircon will contaminate the zirconia. Since zircon is not very soluble in the acids used, it could persist through the process and contribute silica to the analysis of the product.

As the factory increased throughput, samples were selected at periodic intervals and sectioned for microscopic study. The sections were examined for completeness of the reaction, and operating conditions were modified accordingly. By this technique, the production people had more meaningful analytical data, faster, upon which reasoned action could be based. The principle observation from these studies was that an increase in throughput could lead to an increase in unreacted zircon content. This is reasonable, of course. This was also the problem.

The Solution: Microscopy also suggested a solution to the problem. Figure 4 is another view of a partially reacted zircon grain. The picture shows that the grain is surrounded by a coat of reaction products, largely zirconium oxide. For the reaction to continue, it is necessary for CaO to diffuse into the reaction front, and $CaO \cdot SiO_2$ to diffuse back out again. As the coating on the grain becomes thicker, this diffusion process slows down as the molecules have greater distance to

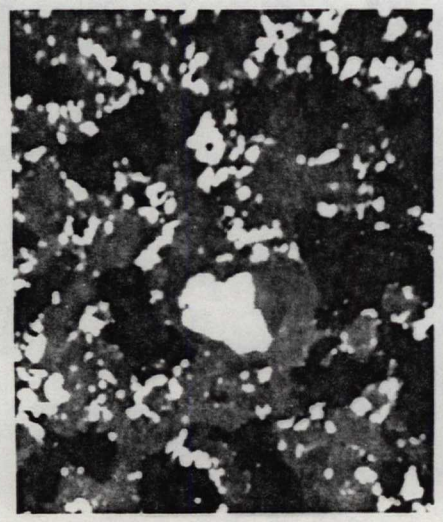

Figure 3: The petrographic microscope shows four phases in this experimental clinker—unreacted zircon, ZrO_2, $CaO \cdot SiO_2$, and pores.

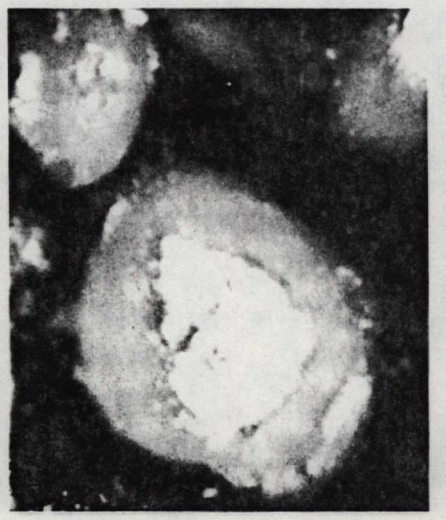

Figure 4: A partially reacted zircon grain surrounded by a coat of reaction products, largely ZrO_2.

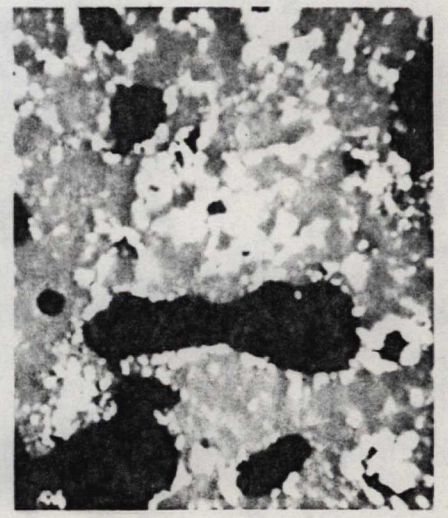

Figure 5: Thin section of completely reacted clinker with white crystals of $CaO \cdot SiO_2$ embedded in and coating a ground mass of fine ZrO_2.

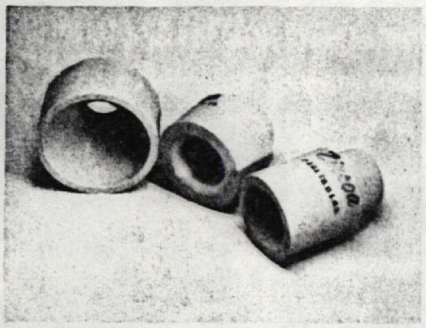

Figure 6: Zirconia tundish nozzles.

travel. Mathematically, we would say that the reaction kinetics are apt to follow a parabolic rate function. We are conducting an experiment to see if this is true. I must confess, however, that the production problem was solved long ago with the aid of microscopy, and the experimental results are still not in and analyzed. This is what often happens in a quick acting small company.

The reaction kinetics can be increased by raising the temperature of the reaction! A plant test was conducted and the premise proven. The higher temperature favored a more complete reaction as was expected, eliminating the prospect of residual zircon under altered operating conditions. Figure 5 shows a thin section of a completely reacted clinker with white crystals of calcium silicate embedded in and coating a ground mass of fine zirconium oxide.

A program was instituted for the plant operative personnel to operate the process at a higher temperature. The photography which you have just examined also convinced all concerned of the problem, and with a suitable increase and attention paid to kiln temperatures, a higher throughput was made possible without sacrificing product quality. Samples of clinker are now being routinely examined to insure continued high quality products.

Case History—II

The Problem: Zirconia tundish nozzles used in the continuous casting of ferrous metals can be used up to eight heats and average four or five heats usable life. While this performance is four to eight times better than competitive materials, there is always the desire to understand the eventual failure and to strive for even better performance if possible. Can we learn anything about the changes which take place during use with microscopy?

One requirement of the continuous casting process for steel is that a steady metal flow must be supplied to the casting process. This means that delivery from a reservoir (tundish) must be regulated through a nozzle that will maintain its internal diameter at 2950°F in contact with a flowing stream of molten steel and metal oxides. Zirconium oxide is a natural for this type of service because of its extreme inertness, refractoriness, and availability. Figure 6 shows a view of this ceramic hardware.

Analytical Examination: A nozzle that had been used for five heats was sectioned and examined microscopically. Figure 7 shows a microscopic view sectioned through the internal diameter of the nozzle. The zirconia is monoclinic with an average grain size of about 10 to 15 microns. Figure 8 is a view sectioned through the exterior of the nozzle. The material is predominantly cubic zirconia with a variable grain diameter as determined by the coarse and fine fractions that were blended and pressed together during fabrication. Some grains are as large as 350 microns.

These two views illustrate that the zirconia loses lime during the casting process. A layer about 1/16" deep is affected. This layer inverts back to the monoclinic zirconia in service, and surprisingly this also results in a breaking up of the coarse cubic grains into a finer microstructure. Microscopy has also revealed that this layer is impregnated with the glassy slag.

The Solution: It appears that the glassy slag is reacting with the zirconia at high temperatures so as to remove the lime content. The zirconia itself is relatively unaffected. The surface layer impregnated with the glass changes from cubic to monoclinic zirconia. Now, this could be harmful to the ceramic. Monoclinic zirconia does not remain stable with temperature. At about 2000°F the monoclinic form changes again to a different crystal structure. In this process, it will shrink in size. You can imagine how this would have disastrous effects on the ceramic, with each grain shrinking different amounts in different directions. I'm sure that your imagination has been vindicated; repeating heating and cooling causes the ceramic to break up. These fractures could be the source of the crack nuclei which are causing the break up of the tundish nozzles. The destructive changes in the nozzle body are long term effects that have not detracted from the advantages of zirconia for this application.

This does illustrate how microscopy can reveal internal changes in microstructure and composition that could cause poor long-term performance. Armed with this knowledge, we are now ready for the next step—the deri-

Figure 7: Microscopic section through internal diameter of a five-heat nozzle.

Figure 8: A section through the nozzle's exterior.

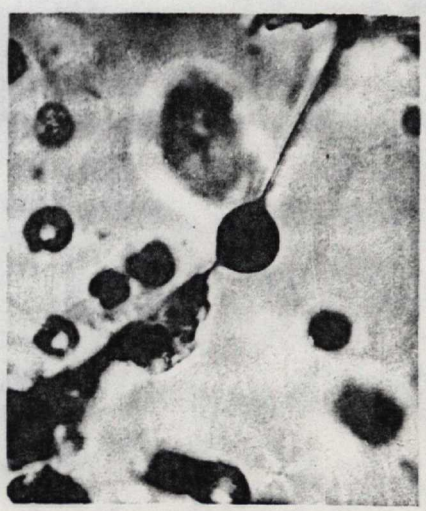

Figure 9: Stabilized ZrO_2 with a pore ideally situated on a grain boundary.

vation of practical remedies to extend the life of these nozzles even further. We do have some ideas.

Case History—III

The Problem: Develop a better understanding about porosity in zirconia ceramics. The pore structure of the ceramic body has to be described by the amount, size, distribution, and shape. Each of these has unique ramifications upon how the ware will function in service. The first step in establishing an increase in control refinement is to develop an understanding of the ceramic's nature. This understanding will be interpreted in terms of firing schedules and batch compositions.

Analytical Examination: Polished thin sections were made of a variety of zirconia materials. The polishing of the sections on both sides is virtually mandatory on materials with a high index of refraction. The optical mis-match between the low index mounting plastic and the high index zirconia causes a serious amount of light scatter, which makes the viewing as though it were through a fog. The extra work is well worth the effort.

Figure 9 is a view of a stabilized zirconia (contains enough lime or other special oxide to cause the structure to crystallize in the cubic system).

The pore shown is where it ideally should be; on a grain boundary. It is round, and additional heat treatment would probably cause it to shrink and finally disappear. Figure 10 shows a view of a grain that contains pores where they are troublesome—assuming that a high density ceramic is specified. Pores within the center of grains are difficult to remove as the contained gases must diffuse out through closely fitting crystal lattices. Figure 11 shows the effect of additional heat treatment, with the pores near the boundaries being removed more easily than those further away in the center of the grains.

Since the starting material is a two micron powder, the pores are not residual effects from the raw materials, but must arise from the sintering and grain growth history of the ceramic during firing. The petrographic microscope is an excellent tool for following this history and directing the selection of fabrication conditions so that the commercial needs of the product are met and maintained. Density measurements by themselves won't do this. They don't say where the pores are; nor do they tell us if additional heat treatment will increase density. This is a job for microscopy.

Theoreticians tell us, and experimenters demonstrate, that pores can act as stress risers in a material. A substance containing pores is likely to be less strong than a substance which is fully dense. The stresses tend to concentrate around irregularities such as pores. The microscope is a tool for seeing these stresses and their patterns.

Any ceramic material as it is cooled builds up stresses at grain boundaries and within the grains. This happens because each grain tends to shrink a little more in one direction than in another, and since they are all jammed together at random, thermal contraction stresses are built up. Figure 12 shows a pore in a zirconia ceramic with an accompanying photoelectric stress pattern. In this material the pores tend to develop shapes that reflect the crystal symmetry of the lattice that contains them. Normally, a pore will be round as this shape has the lowest surface energy. In a crystal, such as in a grain of zirconia, the surrounding lattice modifies the pore to a cubic shape. When this happens the stresses within the grain become concentrated on the sharp corners of the cube. We don't see these stress concentrations on rounded pores—only on those that have polygonized.

The Solution: The tendency for the pore to form a regular crystal shape is determined by heat treatment. We can use the petrographic microscope to detect polygonization, which is harmful, and control the sintering process accordingly. We can also use microscopy to tell us where the pores are in the microstructure. This knowledge aids in the determination of firing schedules.

These are only three examples of petrography as a ceramic control laboratory. These examples do serve to make a point. None of these problems were likely to have been solved without the use of petrography. Polished sections did not provide the necessary information. A zircon in reflected light looks not unlike a zirconia crystal, and while a change in microstructure can be seen by either technique, only transmitted light supplies the information as to what the phases are and where they occur. While a polished section is good for the detection of pore polygonization, it tells us nothing about accompanying stresses. It does not ring the alarm bell that we have a potential problem, and a casual observation would not be translated into corrective action. ■

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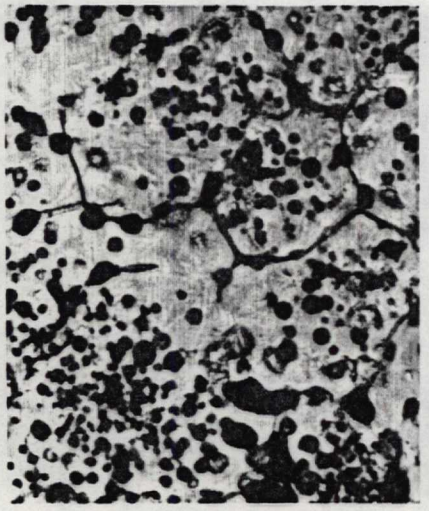

Figure 10: *Stabilized ZrO_2 with undesirably-located pores.*

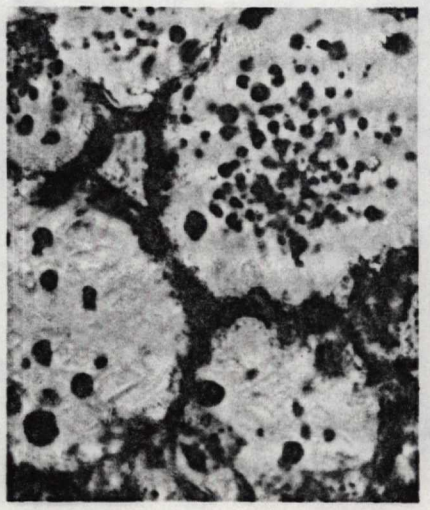

Figure 11: *Additional heat treatment causes removal of some pores.*

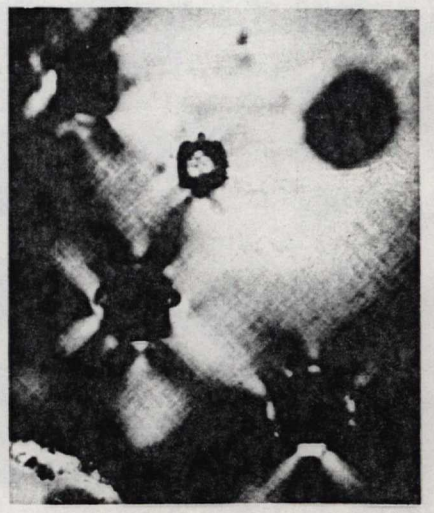

Figure 12: *A pore and its photoelectric stress pattern.*